

# High Throughput Methods for Nanocomposite Materials Research. Extrusion and Visible Optical Probes.

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## INTRODUCTION

A quiet revolution is occurring in the field of polymer science – the high throughput (HT) or combinatorial revolution. It is, in a general sense, a change in the way one views performing research and development, and simply involves devising methods to allow one to carry out many more experiments, per unit time, than was previously possible. It appears that even the methods developed so far are poised to generate the same explosion in information that both the spectroscopic and computerization revolutions brought to all the sciences. Most of the HT methods, which borrow from those developed for drug discovery, use multiple, small-scale sample preparation and analysis techniques, which take advantage of automation, robotics, and either serial or parallel analysis methods. An alternative approach utilizes the concept of a gradient. This involves either a gradient in the composition, or in the conditions of sample preparation, or a gradient in the testing environment. We have focused our HT methods development efforts on these later “gradient-type” approaches.

Our interest in developing HT methods was motivated by the fact that the study of polymer nanocomposites is a multiple parameter-space problem, and the detailed understanding of these materials involves investigation of a large volume of the associated multi-dimensional property space. This multi-dimensional parameter space for polymer-nanocomposites consists of the obvious list of different material types under consideration, such as “polymer” and “nano-additive,” but also includes interphase surface chemistry, surface treatments, and processing conditions. This article presents combinatorial library design and high-throughput screening methods for polymer nanocomposites intended as flame-resistant materials. Several HT methods have successfully been developed in our labs. An overview of these is presented here, along with a specific focus on recent results using an optical probe, the cationic dye Nile Blue A, to characterize intercalation and exfoliation of organo-layered silicates (clays) in polyamide-6 (PA-6).

## APPROACH

In the development of library preparation methods we have two approaches: thermoplastic extrusion, and precision gradient coatings preparation. This later method is only in the initial stages of development, and will not be discussed here. However, our extrusion of polymer libraries has allowed at least a factor of ten improvement in the rate at which we generate samples. This is primarily because we directly extrude our samples required for testing, and therefore avoid the pelletizing and injection molding steps. This has been used to the greatest advantage in evaluating the flammability of polymers. This HT

flammability characterization utilizes measurement of flame spread of samples in the form of rods, or tapes, used directly from the extruder. Two HT flame spread experiments have been developed. Both utilize the gradient approach. The first uses a gradient in the composition of the sample, created by varying the relative feed rates of the feeders during extrusion. The second uses extruded rods of homogeneous composition, and instead evaluates the flame spread in a gradient flux field. A more detailed discussion of these HT flammability methods has recently been published.<sup>1</sup> We have found this later approach, using a gradient in the testing environment, to be extremely powerful and hope to expand on this theme in other HT methods.

Once methods are in hand to rapidly prepare libraries of samples the challenge shifts to rapid, quantitative evaluations of two types: *material characterization* – to determine the “structure” of the samples, and *properties characterization* – to determine the performance of the samples. Above, mention was made of HT flammability *property characterizations*; in the development of HT *materials characterization* methods we focus on both off-line and on-line characterization techniques. An on-line HT *materials characterization* method has been developed using a dielectric spectroscopic slit-die cell, which attaches to the end of the extruder.<sup>2,3</sup> This work will be covered by another paper in this symposium.

Motivated by the inherently labor intensive nature of conventional nanocomposite characterization techniques, the focus is on faster and more quantitative methods for characterization. Specifically, the polymer layered-silicate interactions on the nano-scale (interphase region) and the homogeneity of mixing on both the nano and micro scale. An off-line NMR method has been developed, which, in half the time it takes to do TEM, can quantify the amount of interphase polymer on the surface of the clay and quantify the level of dispersion of the clay on the micro scale.<sup>4</sup>

Recently, another method for probing the interphase region has been developed. The method utilizes a cationic dye, Nile Blue A, to provide both a visible method for following exfoliation, and also a fluorescence phenomenon which correlates with intercalation and exfoliation.<sup>5</sup>

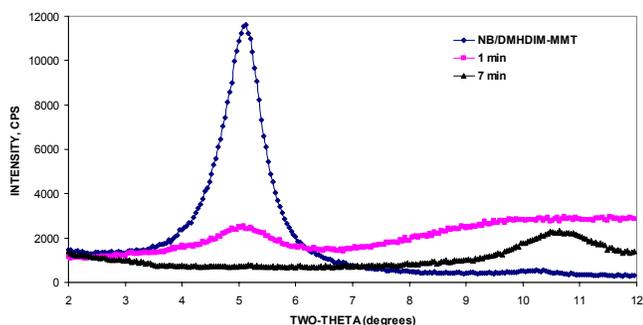
## EXPERIMENTAL<sup>6</sup>

Using standard cation exchange techniques a sodium montmorillonite (MMT) clay was treated with Nile Blue A and a high temperature stable trialkyl imidazolium-based cation (from dimethyl hexadecyl imidazolium BF<sub>4</sub> salt, DMHDIM), in a mass fraction ratio of 1:9, dye to imidazolium. The purified organo-dyed-MMT clay, designated NB-DMHDIM-MMT, was characterized by x-ray diffraction (XRD, Figure 1) and thermal gravimetric analysis (TGA).<sup>5</sup> The NB-DMHDIM-MMT was melt compounded with PA-6 (at 240°C, mass fraction of 2 %, NB-DMHDIM-MMT) in a DACA mini-extruder for two different recirculation times, 1 min and 7 min.

## DISCUSSION

When developing any new analytical method, high throughput or otherwise, validation of the new method requires complete characterization of the subject material using the conventional methods, as well as the new method. This validation process makes the initial development of HT methods a low throughput process.

Complete characterization of the PA-6/NB-DMHDIM-MMT samples (1 min and 7 min) was accomplished using the conventional nanoscale measurement tools, TEM and XRD, and also using the recently developed NMR method.<sup>4,7</sup> All of these methods found that the sample extruded for 1 min had a microcomposite/intercalated morphology. This is evident from the XRD shown in Figure 1. The TEM (not shown) and NMR (not shown) indicate that the sample is comprised of multi-layer (5 to 20) stacks of MMT. This sample has a purple color following extrusion (Figure 2).



**Figure 1.** XRD of the organo-dyed-MMT clay: NB-DMHDIM-MMT, and both extruded samples of PA-6/NB-DMHDIM-MMT (1 min and 7 min). The sample after 1 min appears to contain unchanged NB-DMHDIM-MMT, whereas the 7 min sample has no peak from the organo-dyed-MMT and shows the peak characteristic of the  $\gamma$ -form of PA-6 at  $10.8^\circ$  ( $2\theta$ ).<sup>8</sup>



**Figure 2.** Color images of PA-6/NB-DMHDIM-MMT (mass fraction 2 %) mixed in a DACA mini-extruder for 1 min (top) and 7 min (bottom). The top (purple) sample is a mixture of microcomposite and intercalated MMT, according to TEM, XRD and NMR; and the bottom (red) sample is a mixed disordered intercalated and exfoliated morphology according to TEM, XRD and NMR.

In contrast, TEM, XRD and NMR reveal that the sample extruded for 7 min has a far more exfoliated structure, with individual MMT layers uniformly distributed in the PA-6. This sample is bright red

following extrusion. Figure 2 shows images of both extrudates. The original NB-DMHDIM-MMT is a blue powder as is the control mixture of Nile Blue A compounded into PA-6. One possible explanation for this red color in the PA-6/NB-DMHDIM-MMT is that as the layers separate the effective concentration of NB decreases, which reduces the dye-dye interactions that cause concentration quenching of fluorescence. Presumably, the 1 min sample is purple from a mixture of unchanged NB-DMHDIM-MMT (blue) and disordered intercalated or exfoliated NB-DMHDIM-MMT (red). Indeed, laser induced fluorescence (LIF) measurements show that this color change is also accompanied by fluorescence at 605 nm (red) which grows in intensity as the clay exfoliates.<sup>5</sup> The point we wish to emphasize here is that this “dye-clay” method appears to offer the potential for a very simple *color change* method for monitoring exfoliation, possibly - online during extrusion of HT nanocomposite libraries. We plan to set up just such a system capable of quantitative visible spectroscopic characterization online.

This approach should be applicable to characterization of other nanocomposites by using dye-tagged carbon nanotubes, nanosilicas and polyhedral oligosilsesquioxanes (POSS).

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6. This work was carried out by the National Institute of Standards and Technology (NIST), an agency of the U. S. government, and by statute is not subject to copyright in the United States. Certain commercial equipment, instruments, materials, services, or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.
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8. The uncertainty (one sigma) in  $2\theta$  is  $\pm 0.1^\circ$  and is determined from running a standard sample of Na MMT multiple times.